PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

REC'D 23 MAY 2006

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Applicant's or agent's file reference FP20890	**FOR FURTHER ACTION**	See Form PCT/IPEA/416
International application No. **PCT**/AU2005/000033	International filing date *(day/month/year)* 13 January 2005	Priority date *(day/month/year)* 15 January 2004

International Patent Classification (IPC) or national classification and IPC

Int. Cl.

H03B 7/06 (2006.01) ***H04R 17/00*** (2006.01)

Applicant

THE UNIVERSITY OF SYDNEY et al

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 4 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. [X] *(sent to the applicant and to the International Bureau)* a total of **8** sheets, as follows:
      - [X] sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
      - [ ] sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.
   b. [ ] *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or table related thereto, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).
4. This report contains indications relating to the following items:

[X]	Box No. I	Basis of the report
[ ]	Box No. II	Priority
[ ]	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
[ ]	Box No. IV	Lack of unity of invention
[X]	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
[ ]	Box No. VI	Certain documents cited
[ ]	Box No. VII	Certain defects in the international application
[X]	Box No. VIII	Certain observations on the international application

Date of submission of the demand 26 July 2005	Date of completion of this report 08 May 2006
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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
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Box No. I **Basis of the report**

1. With regard to the **language**, this report is based on:

[X] The international application in the language in which it was filed

[ ] A translation of the international application into , which is the language of a translation furnished for the purposes of:

[ ] international search (under Rules 12.3(a) and 23.1 (b))

[ ] publication of the international application (under Rule 12.4(a))

[ ] international preliminary examination (Rules 55.2(a) and/or 55.3(a))

2. With regard to the **elements** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

[ ] the international application as originally filed/furnished

[X] the description:

pages **1-4, 6-9, 12-35, 37** as originally filed/furnished

pages* **36, 38** received by this Authority on **7 September 2005** with the letter of **6 September 2005**

pages* **5, 10, 11** received by this Authority on **31 March 2006** with the letter of **the same date**

[X] the claims:

pages **42** as originally filed/furnished

pages* as amended (together with any statement) under Article 19

pages* **39-41** received by this Authority on **31 March 2006** with the letter of **the same date**

pages* received by this Authority on with the letter of

[X] the drawings:

pages **1/8-8/8** as originally filed/furnished

pages* received by this Authority on with the letter of

pages* received by this Authority on with the letter of

[ ] a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing.

3. [ ] The amendments have resulted in the cancellation of:

[ ] the description, pages

[ ] the claims, Nos.

[ ] the drawings, sheets/figs

[ ] the sequence listing *(specify)*:

[ ] any table(s) related to the sequence listing *(specify)*:

4. [ ] This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

[ ] the description, pages

[ ] the claims, Nos.

[ ] the drawings, sheets/figs

[ ] the sequence listing *(specify)*:

[ ] any table(s) related to the sequence listing *(specify)*:

* *If item 4 applies, some or all of those sheets may be marked "superseded."*

Box No. V **Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Claims	**1-22**	**YES**
	Claims	**nil**	**NO**
Inventive step (IS)	Claims	**1-22**	**YES**
	Claims	**nil**	**NO**
Industrial applicability (IA)	Claims	**1-22**	**YES**
	Claims	**nil**	**NO**

2. Citations and explanations (Rule 70.7)

NOVELTY (N) and INVENTIVE STEP (IS)

Neither of the citations in the International Search Report disclose a crystal controlled oscillator wherein the crystal is formed from a material other than quartz and wherein the thermal expansion characteristic of the material itself enables temperature dependence of the oscillator frequency to be controlled over an operating temperature range for the oscillator. Therefore independent claims 1, 14 and 16 which define these features, and dependent claims 2-13, 15, 17-22, are novel and involve an inventive step.

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

Claim 1 lacks clarity because:

1) it is not fully clear what is meant by the phrase "that is suitable for use in the oscillator"

2) it is not fully clear what is meant by the term "the thermal expansion characteristic of the material itself enables temperature dependence.... to be controlled".

Claim 3 lacks clarity because:

1) it is directed to "an oscillator as claimed in claim 1 or 2" but claim 2 defines a timing device not an oscillator.

2) it defines that the thermal expansion characteristic is anisotropic or isotropic but surely it can only be anisotropic or isotropic so the claim does not define anything.

In Table 1:

- the C value represents a mechanical property of the crystal, namely, its elastic constant, which is related to Young's Modulus;

- the d value represents the piezoelectric coefficient (charge/force or C/N) which indicates the crystal's piezoelectric effect;

- the ϵ value represents the dielectric constant, which is also related to the piezoelectric effect;

- the k value represents the coupling coefficient which is derived from a measurement of resonance frequency, and which is related to the oscillator performance Q of the crystal (also see Table 2 below).

In Table 1 the references 11, 12 etc through to 66, refer to the crystal axis along which the measurement is taken.

From these results, it can be seen that the material $KMn[Ag^{I}(CN)_2]_3$ has a coupling coefficient which is better than that of quartz (quartz has a $k_{11} = 0.102$). This demonstrates that $KMn[Ag^{I}(CN)_2]_3$ displays a better piezoelectric effect than the standard oscillator crystal quartz. In addition, the mechanical properties and oscillator performance of $KMn[Ag^{I}(CN)_2]_3$ are comparable to that of quartz, indicating that $KMn[Ag^{I}(CN)_2]_3$ can be used in place of quartz in a crystal oscillator.

Reference will now be made to Table 2. Table 2 presents the results of testing additional samples of $KMn[Ag^{I}(CN)_2]_3$ for resonance frequency:

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using $KMn[Ag^{I}(CN)_2]_3$).

Any reference herein to a prior art document or use is not an admission that the document or use forms part of the common general knowledge of a skilled person in this field in Australia or elsewhere.

Whilst a number of specific material embodiments have been described, it should be appreciated that the material and resulting oscillators may take many other forms.

had then unforeseen properties that might enable the materials to be employed in a crystal oscillator.

Summary of the Disclosure

In a first aspect there is provided a crystal-controlled oscillator, the crystal being formed from a material other than quartz and that is suitable for use in the oscillator, characterised in that the thermal expansion characteristic of the material itself enables temperature dependence of the oscillator frequency to be controlled over an operating temperature range for the oscillator.

In a second aspect there is provided a timing device incorporating the crystal-controlled oscillator of the first aspect.

The applicant has discovered and developed certain materials suitable for use as a crystal in an oscillator that have an intrinsic expansion characteristic that allows for intrinsic control of the temperature dependence of oscillator frequency (ie. without the need for any compensation external to the material or oscillator).

For example, crystals can be formed that, over an operating temperature range for the oscillator, have a thermal expansion characteristic that is zero or near zero, or that display expansion that has a negligible effect on the temperature dependence of oscillator frequency. Thus, the dependence of oscillator frequency on temperature can be substantially eliminated or be negligible, so that the elaborate temperature compensation configurations of the prior art can be avoided.

Notably, the thermal expansion characteristics of known oscillator materials (such as quartz) are not themselves adapted to enable the temperature dependence of oscillator frequency to be controlled over an operating

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manufacturing temperature ranges for crystal-controlled oscillators.

Suitable materials herein can be grown as single crystals to typical size ranges for crystal-controlled oscillators (eg. from 1mm up to and beyond 5mm in diameter, length and/or width). Crystal growth may occur by slow diffusion at ambient temperature or by solvothermal synthesis at higher temperatures. Both of these techniques are substantially simpler and cheaper than known techniques used to grow quartz crystals.

Suitable materials herein may have a piezoelectric effect at least comparable to quartz and in some cases greater. Where the effect is less than quartz, the only drawback noted is that the oscillator can draw more power.

Suitable crystalline materials herein comprise a plurality of diatomic bridges, the or each bridge extending between two atoms in the material, with the or each diatomic bridge having at least one vibrational mode that causes the two atoms on either side of the bridge to be moved together to the same extent as competing vibrational mode(s) that cause the two atoms on either side of the bridge to be moved apart. Such a material displays zero thermal expansion (ZTE) behaviour.

Suitable crystalline materials herein include: $Zn^{II}[Ag^{I}(CN)_2]_2.0.575\{AgCN\}$, $Zn^{II}[Au^{I}(CN)_2]_2$, $KCd^{II}[Ag^{I}(CN)_2]_3$, $KMn[Ag^{I}(CN)_2]_3$ and $KCd^{II}[Au^{I}(CN)_2]_3$, which display both ZTE along at least one axis and a piezoelectric effect.

Alternatively, the crystalline material can have either a negative thermal expansion characteristic or a positive thermal expansion characteristic, but in either case modified (eg. doped) to have ZTE.

In a third aspect there is provided the use of a material other than quartz in a crystal-controlled

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oscillator, characterised in that the thermal expansion characteristic of the material itself enables temperature dependence of the oscillator frequency to be controlled over an operating temperature range for the oscillator.

The crystal-controlled oscillator of the third aspect can be used in a timing device.

In a fourth aspect there is provided a method of fabricating a crystal for an oscillator from a piezoelectric material other than quartz having a thermal expansion characteristic that enables temperature dependence of the oscillator frequency to be controlled over its operating temperature range, the method comprising the step of cutting the material in a manner that imparts to an oscillator formed therefrom a near zero, negligible or simple frequency dependence over its operating temperature range.

The crystal can also be formed to have a zero or near zero thermal expansion characteristic along at least one axis therethrough.

The crystal can be grown by slow diffusion at ambient temperature or by solvothermal synthesis at temperatures higher than ambient. During crystal growth, the thermal expansion properties of the crystal can be modified by selective doping of metal sites, modification of guest molecules, modification of counter-ions, and/or by altering the degree of interpenetration of material topology. After crystal growth, the thermal expansion properties of the crystal can be optimised by cutting the crystal along a direction in which the material has a ZTE characteristic, or a characteristic closely approaching ZTE.

Brief Description of the Drawings

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Claims

1. A crystal-controlled oscillator, the crystal being formed from a material other than quartz and that is suitable for use in the oscillator, characterised in that the thermal expansion characteristic of the material itself enables temperature dependence of the oscillator frequency to be controlled over an operating temperature range for the oscillator.

2. A timing device incorporating the crystal-controlled oscillator of claim 1.

3. An oscillator as claimed in claim 1 or 2 wherein the thermal expansion characteristic is anisotropic or isotropic.

4. An oscillator as claimed in any one of the preceding claims wherein the thermal expansion characteristic of the material is adapted by tuning the coefficient of thermal expansion of the material.

5. An oscillator as claimed in claim 4 wherein tuning is achieved by:

(1) modifying the composition of the crystal; and/or

(2) cutting the material along a direction that has zero or near zero thermal expansion (ZTE).

6. An oscillator as claimed in any one of the preceding claims wherein the operating temperature range in which controlled thermal expansion is maintained is from -200°C to +150°C.

7. An oscillator as claimed in claim 6 wherein the operating temperature range in which controlled thermal expansion is maintained is from -55°C to +125°C.

8. An oscillator as claimed in any one of the preceding claims wherein the material is formed from a crystalline material comprising a plurality of diatomic bridges, each diatomic bridge extending between two atoms in the

material, and each diatomic bridge having at least one vibrational mode that causes the two atoms on either side of the bridge to be moved together to the same extent as competing vibrational mode(s) that cause the two atoms on either side of the bridge to be moved apart.

9. An oscillator as claimed in claim 8 wherein the material comprises a plurality of linear and/or non-linear diatomic bridges.

10. An oscillator as claimed in claim 9 wherein the material comprises linear cyanide -(CN)- bridges and/or non-linear cyanide bridges.

11. An oscillator as claimed in any one of the preceding claims wherein the material is: $Zn^{II}[Ag^{I}(CN)_2]_2.0.575\{AgCN\}$, $Zn^{II}[Au^{I}(CN)_2]_2$, $KCd^{II}[Ag^{I}(CN)_2]_3$, $KMn[Ag^{I}(CN)_2]_3$ or $KCd^{II}[Au^{I}(CN)_2]_3$.

12. An oscillator as claimed in any one of the preceding claims wherein the thermal expansion characteristic of the material is modified by one or more of:

- selective doping of any metal sites present in the material;
- modification of guest molecules in the material;
- modification of counter-ions in the material; and/or
- by altering the degree of interpenetration of material topology.

13. A crystal for an oscillator substantially as herein described with reference to the Examples and/or the accompanying drawings.

14. The use of a material other than quartz in a crystal-controlled oscillator, characterised in that the thermal expansion characteristic of the material itself enables temperature dependence of the oscillator frequency to be controlled over an operating temperature range for the oscillator.

15. The use as claimed in claim 14 that is use of the oscillator in a timing device.

16. A method of fabricating a crystal for an oscillator from a piezoelectric material other than quartz having a thermal expansion characteristic that enables temperature dependence of the oscillator frequency to be controlled over its operating temperature range, the method comprising the step of cutting the material in a manner that imparts to an oscillator formed therefrom a near zero, negligible or simple frequency dependence over its operating temperature range.

17. A method as claimed in claim 16 wherein the piezoelectric material is formed to have a zero or near zero thermal expansion characteristic along at least one axis therethrough.

18. A method as claimed in claim 16 or 17 wherein a crystal of the piezoelectric material is grown by slow diffusion at ambient temperature or by solvothermal synthesis at temperatures higher than ambient.

19. A method as claimed in any one of claims 16 to 18 wherein, during formation of the piezoelectric material, the thermal expansion characteristic of the material is modified by selective doping of metal sites, modification of guest molecules, modification of counter-ions, and/or by altering the degree of interpenetration of material topology.

20. A method as claimed in any one of claims 16 to 19 wherein, after formation of the piezoelectric material into a crystal, the thermal expansion properties of the crystal are optimised by cutting the crystal along a direction in which the material has a zero thermal expansion (ZTE) characteristic, or a characteristic closely approaching ZTE.